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THE COMMON AND SYSTEMATIC NOMENCLATURE OF CYCLIC DITERPENES

Prepared by

JOHN W. ROWE

Cosponsored by:

J. ApSimon, M. Fétizon, E. Fujita, L. Gough, W. Herz, P. R. Jefferies, D. Mangoni, T. Norin, K. Overton, S. W. Pelletier, and E. Wenkert

Third Revision

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Introduction

The need for a unifying systematic nomenclature for diterpenes is readily apparent. Current practices are often chaotic, and although attempts at systematic nomenclature have been incorporated into the papers of numerous authors, these differ from one another with the result that the literature is becoming rapidly cluttered with nomenclature practices using a variety of skeletons, numbering systems, and methods of designating modifications. The assignment of common names to new, naturally occurring diterpenes is resulting in a proliferation

[1]Maintained in cooperation with the University of Wisconsin.

of names which, with the current rapid progress in diterpene chemistry, promises soon to get out of hand.

Our initial attempt toward systemization of diterpene nomenclature was distributed in the fall of 1966 to a few people working in the field. Based upon the comments received, a more detailed proposal was distributed in April 1967. A Second Revision dated April 1968 was the subject of an extended discussion arranged by Dr. L. C. Cross as part of the 5th International Symposium on the Chemistry of Natural Products held in London during July 1968. Approximately 40 participants reviewed these proposals, and a number of changes were made. This third revision should now be very close to the final form. It is expected that after approval by the cosponsors, possibly with a few further minor revisions, it will be submitted to the IUPAC Commission on Organic Nomenclature.

Professors Fétizon and Le Van Thoi's book on the cyclic diterpenes (Holden-Day) is now scheduled to be submitted to the publisher in the summer of 1969. Professor Fétizon states that he wants to use this nomenclature system throughout the book, and will publish the nomenclature rules as an appendix to the book.

We are grateful for the large number who expressed agreement with, and support of, the nomenclature suggestions. Even more valuable has been the large number of criticisms, corrections, and suggestions. To expedite this revision, no response has been made by the author to many of

the respondents, but all comments have been carefully evaluated. In this revision, the suggestions detailed herein represent the most systematic synthesis from various viewpoints.

This revision is being sent to all those listed in the appendix.

Common Names

The informational content of common names is rather limited, and further proliferation of these should be avoided insofar as practical. Numerous common names are quite misleading, and some natural products have two or more common names. Levopimaric acid is not a pimaric acid. Sandaracopimaric acid should actually be epipimaric acid. However, it is recognized that common names such as these are too commonly accepted to be changed without multiplying the confusion, especially in the older literature. In the case of the resin alcohols, abietol, pimarol, dehydroabietol, and so forth, it should be noted that Wenkert has pointed out that these are the correct form. Abietinol, pimarinol, dehydroabietinol, and others, are derived from the German (e.g., Abietinsaüre).

The following rules are suggested as a guide in the naming of new diterpenes. However, it is recommended that names already given to known diterpenes be retained unless confusion exists.

1. Where possible, only systematic names should be used for synthetic products or for alteration products of known natural products. Thus the

product of hydrogenation of manool should be referred to as "13-labdanol" or as "the hydrogenation product of manool" (usually clarified by reference to a structural formula), but not as tetrahydromanool which is not a natural product.

2. The generation of new common names for newly discovered natural diterpenes should be avoided when convenient, and should in no case be reported in the literature until something is known about the structure. The use of the systematic name alone for new diterpenes is recommended.

3. When the systematic name is inconvenient, common names related to known natural products are preferable (e.g., agathic acid, agatholic acid, agatholal, isoagatholal, agathadiol, etc.). To avoid confusion with systematic nomenclature, however, no numbers should be used in such common names except to designate the addition of new functional groups as in 6β-acetoxyozic acid and 6-oxocativic acid. Thus it would have been preferable if larixol had been named 6α-hydroxyepimanool; but as already stated revision of common names already accepted is recommended only in cases where confusion exists. Common names should indicate functionality if possible.

4. When a new natural product has an inconvenient systematic name and is unrelated to other diterpenes, a name based on botanical origin is satisfactory. Diterpenes with common names of botanical derivation

are often found to be widely occurring, and such a name therefore will carry information content only on its original source. Common names should not be based on the common name for the source.

5. Separate common names for optical antipodes are to be avoided. Moreover, the use of "(+)" and "(—)" is to be avoided for common names since their use can be misleading, especially where derivatives of a (+) compound can be levorotatory. Further, in compounds with a low rotation, the sign may be incorrectly measured or actually change with solvent or temperature. Isopimaric acid (69) is a good example of this.

Therefore, if a diterpene is found (or synthesized) which is enantiomeric with a previously suitably named diterpene, it shall be given the same name as the known diterpene, but with a prefix to indicate that it is the optical antipode. If the new diterpene belongs to the enantiomeric series, the common name is merely prefixed by "ent-" as will be the case with the systematic name.

However, if the new diterpene belongs to the normal series or the absolute stereochemistry is unknown, the original common name is to be prefixed by "anti-." "Anti-" is not italicized to avoid confusion with the past use of "anti" with oximes ("E" and "Z" are now preferred to designate the stereochemistry of this type of compound) and compounds such as trans-anti-trans-perhydrophenanthrenes (now named trans-transoid-trans-perhydrophenanthrenes according to the new IUPAC draft rules). If a common name

prefixed by "anti-" is later shown to represent a compound in the enantiomeric series, the prefix of the common name can be readily changed to "ent-" without confusion in the literature. Thus, in most cases common names prefixed by "anti-" will represent diterpenes of the normal series enantiomeric to a previously reported diterpene.

The tetracyclic diterpenes belong predominately to the enantiomeric series. If the optical antipode of steviol, for example, were to be found, the new antipode should not be given the name of steviol while the original diterpene should not be changed to ent-steviol. The result would be extraordinarily confusing in following the literature. Therefore, the new antipode of steviol would be named "anti-steviol."

Preferred common names are given for the illustrations at the end of this proposal. Less preferable common names are given in parentheses. When two diterpenes with different common names are later shown to be enantiomeric, other points being equal, the older name shall have priority and the newer name shall be replaced by the older name plus the appropriate prefix. Thus the name "lambertianic acid" is dropped in favor of "anti-daniellic acid."

It should be pointed out that for the great majority of diterpenes, only one optical antipode is known so that no prefix is required. Further, the actual optical rotation of any diterpene should be readily locatable in the experimental section of the publication as can other such physical constants.

Systematic Names

It is recognized that systematic names are not always the most practical for everyday use as is the case with many IUPAC names, but written communications are best served when every individual compound has a unique and definitive systematic name with maximum informational content for the unspecialized organic chemist.

The numbering of the parent skeletons conforms as closely as possible to common usage, and is analogous to that used for the steroids. Except as noted, IUPAC rules (2) are followed. Generally the rules also conform to the unpublished IUPAC/IUB 1967 Revised Tentative Rules for Steriod Nomenclature and the IUPAC 1968 Tentative Rules, Section E, Fundamental Stereochemistry.

Some diterpenes, such as mutilin (3), eremolactone (4), phorbol (34), ryanodol (45), and the ginkolides (5), cannot be named according to the rules postulated herein. At present they are merely treated as exceptions; but if it appears that compounds of these types may be more common, new skeletons such as mutilane, eremane, and ginkane should be created. The skeleton "tigliane" recommended for phorbol (34) is not adopted in this report. Biflorin (40) is another exception, but this isopentenyl homolog of mansonone F (64) can be readily named according to present IUPAC rules "6,9-dimethyl-3-(4-methyl-3-pentenyl)-1-oxaphenalene-7,8-quinone." Likewise,

alicyclic diterpenes such as vitamin A and geranylgeraniol (65) can be readily named by existing rules.

The new systematic nomenclature now proposed may be used only if it results in a simplification over the current IUPAC nomenclature. Thus retene should be named "7-isopropyl-1-methylphenanthrene" rather than "19,20-dinorabieta-1,3,5(10),6,8,11,13-heptaene," but simonellite (26) is named "20-norabieta-5(10),6,8,11,13-pentaene" rather than "7-isopropyl-1,1-dimethyl-1,2,3,4-tetrahydrophenanthrene." See also tanshinone I and cryptoshinone under ABIETANE.

When two or more systematic names can be chosen for the same compound, preference shall be given to the simpler name. If the systematic names are equivalent in this respect, the choice shall be made between them on biogenetic considerations. In the case of the trachylobanes, names based on ATISANE, BEYERANE, and KAURANE are almost equally simple, and biogenetically they areequally suitable. However, since ATISANE is the shortest (simplest), trachylobanes should be named with this skeleton as has been done. Likewise, nimbiol should be named "12-hydroxy-13-methyl-8,11,13-podocarpatrien-7-one" rather than "12-hydroxy-16,17-dinorabieta-8,11,13-trien-7-one." Ring C aromatic PODOCARPANES, ABIETANES, and CASSANES should likewise be "8,11,13-trienes" rather than the equivalent but more complicated "8(14),9(11),12-trienes."

General Structure of Names

A name is composed of the following items in the order given:

1. A prefix, if needed, to indicate whether the compound belongs to the normal, enantiomeric, or racemic series.

2. Detachable prefixes giving the location, stereochemistry if necessary, and type of substituent groups present marshaled in alphabetical order.

3. Nondetachable prefixes designating modification of the parent structure together with their locants marshaled in the order: aza, cyclo, homo, nor, oxa, seco, abeo, and friedo (i.e., alphabetical except for abeo and friedo which must be directly before the stem name).

4. Designation of the stereochemistry at carbon atoms in the parent skeleton which are epimerized, listed in numerical order.

5. The stem of the name for the parent hydrocarbon.

6. Designation of the degree, position, and stereochemistry (when applicable) of unsaturation.

7. A suffix designating the principal functional group according to IUPAC rules.

1. Normal, Enantiomeric, or Racemic Series

The skeletons chosen are defined as belonging to the normal series. Diterpenes having such absolute stereochemistry, or a stereochemistry in which less than half of the asymmetric centers in the parent skeleton

(before modification by nondetachable prefixes) are inverted, shall have no prefix designating absolute stereochemistry. Diterpenes in which more than half of the asymmetric centers in the parent skeleton are inverted are defined as belonging to the enantio series and shall have a prefix "ent-" at the very beginning of the name. The remainder of the systematic name shall be that of its optical antipode. In the event that exactly half of the asymmetric centers of the parent skeleton are inverted, the stereochemistry of C-20 (C-17 in ACONANE, C-19 in TAXANE) shall be decisive. In diterpenes wherein unsaturation removes one or more of the asymmetric centers in the parent skeleton, the above rule will be applied only to the unaffected centers.

Racemates, as for instance obtained by synthesis, are named by the use of the prefix "rac-" (an abbreviation of racemo) at the beginning of the complete name of the compound with the stereochemistry of the normal series.

Diterpenes of unknown absolute configuration shall be prefixed by "rel-", indicating that only relative configurations are given. This is taken from the IUPAC tentative rules. When both enantiomers of known relative, but unknown absolute, configuration are known, they are distinguished by a prefix "(+)-rel-" or "(—)-rel-," where the plus or minus sign refers to the direction of rotation.

of plane-polarized light (the wavelength, solvent, temperature, and/or concentration must be added when known to affect this sign).

2. Detachable Prefixes Locating Substituents

Standard IUPAC rules are followed. Fused ring systems unless otherwise designated are considered to be in the plane of the paper. Groups projecting above this plane are indicated by a heavy line and designated "β." Groups projecting below this plane are indicated by a dotted line and designated "α." It has been suggested that configuration at centers in the side chain be designated according to the α, β convention of the Fieser-Plattner method (6). However, because of the occurrence of cyclized derivatives, the R and S convention (7) is preferable for designating the stereochemistry at positions in side chains. However, the R and S designation at C-13 in LABDANE is undesirable, since biogenetically there are two distinct series and modification of C-14 and C-16 can change the R and S assignments even within one series. Furthermore, the LABDANE skeleton carries the absolute stereochemistry at C-13 with it.

An example of the difficulties inherent in using R and S at C-13 in LABDANE can be illustrated by labdanolic and eperuic acids. In both compounds C-13 is actually S (ent-13R in eperuic acid). However, the parent hydrocarbon of both is R. Thus it is understandable that a recent publication (46) reported that labdanolic and eperuic acids had the 13R configuration when the 13S configuration was actually illustrated.

It should be noted that replacement of a tertiary hydrogen by another group is always with retention of stereochemistry, so no stereochemical designation is needed, as for example, with the 8,13-diol of sclareol; this information is already designated by the skeletal name.

Unknown configuration, whether in a side chain or a ring, is indicated by "ξ". Two epimers of unknown configuration are indicated by "ξ_1" and "ξ_2." Unknown position of substitution (which includes unknown stereochemistry) is indicated by the use of "x" for the first, "y" for the second, and so forth. Letters should follow numbers if both precede the same prefix.

The prefix "epoxy" is used to designate ring closure through an ethereal atom of oxygen. The two locants give the carbon atoms to which this oxygen is bound. According to current IUPAC rules, the prefix "epoxy" indicates an oxygen atom directly attached to two carbon atoms already forming a part of a ring or to two adjacent atoms in a chain. Consequently, the usage proposed herein extends the use of the prefix "epoxy" to include even oxygen bridges between nonadjacent atoms of the side chains.

3. Nondetachable Prefixes Designating Modification of Parent Structure

All of these prefixes should be preceded by "di," "tri," and others, with the appropriate locants separated by colons if the skeletal modification occurs more than once. If more than one type of skeletal modification or more than two modifications of any one type are required,

consideration should be given to the creation of a new skeleton. The suggestion to incorporate Barton's "abeo" as used in steroid nomenclature is enthusiastically accepted. The suggestion to use Ourisson's (8) "friedo" is adopted in modified form. Although this prefix does not seem to have been widely used, it has obvious advantages over the x-homo-y-nor nomenclature. Modifications using "abeo" are preferred to those using "nor" and "homo" together; the latter in turn is preferred to those using "seco" and "cyclo" together.

The use of small capital letters to locate the "nor" and "homo" modifications as in current steroid nomenclature is not recommended because of the larger number of alkyl side chains and the more complicated ring junctions in diterpenes.

"Aza-" and "oxa-" indicate replacement of a carbon atom in the ring system together with its accompanying hydrogens by nitrogen (or NH) or oxygen as usual.

Cyclo.--This designates the formation of a single bond between the two atoms of the parent structure designated by the locants with the simultaneous loss of a hydrogen from each of the atoms. If the hydrogen is lost from a methylene group, designation of the stereochemistry of the "cyclo" bond at this carbon atom is required unless only one stereochemistry is possible. If the hydrogen is lost from a methyl group, no designation of stereochemistry is required; if from a methine group, designation of

stereochemistry is required only if it is different from that of the methine hydrogen (see section 4).

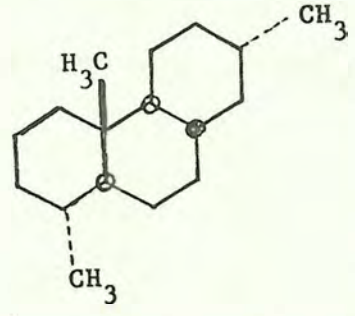
Homo.--This indicates addition of a methylene group to a ring or side chain of the parent skeleton. It should not be applied to the addition of a methyl or other alkyl group which can be readily named according to existing rules. The configuration and numbering of the modified skeleton are unaltered except that the added methylene is assigned number "xa" (and "xb" for dihomo when ethylene is added, etc.) where "x" is the lower number of the two adjacent carbon atoms. The locant preceding "homo" consists of the two numbers of the adjacent carbon atoms, the highest alternatives being chosen if there are alternative possibilities.

Nor.--This indicates elimination of a carbon methyl or methylene group from the parent structure. When a methyl is eliminated, it is replaced by hydrogen of the same stereochemistry. When a methylene is eliminated, the resulting pendent valencies are joined. The locant preceding the prefix gives the number, or the highest of the permissible alternatives, of the carbon atom eliminated. The numbering of the resulting skeleton is unaltered except for deletion of the number corresponding to the deleted carbon.

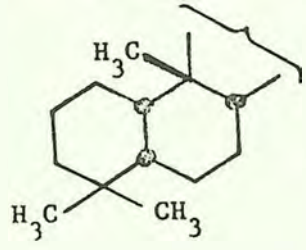
Seco.--This designates bond rupture between two atoms of the parent structure with simultaneous addition of hydrogen to each of the two atoms. The location of this structural modification is again given by the preceding pair of locants.

Abeo.--When a bond joining one carbon atom to a second carbon atom has been broken and a new bond formed between the first carbon atom and a third carbon atom rather than A-homo-B-nor or a,c-cyclo-a,b-seco type of nomenclature, the prefix "abeo" shall be used. The locants preceding this shall be of the form "a(b → c)." Hydrogen is added to the pendent b valency, and the stereochemistry and numbering are not altered in this transformation unless otherwise designated. If c is a methylene group, the stereochemistry of c shall be indicated by adding "αH," "βH," or "ξH" immediately after the locant representing c. If c is a methine group, the stereochemistry shall be indicated by "R," "S," or "ξ."

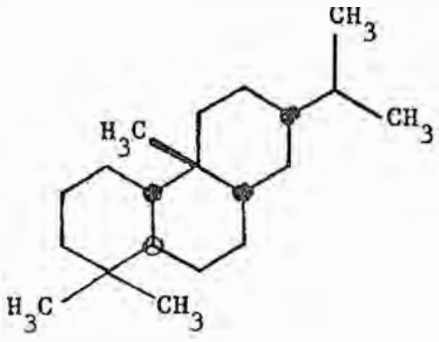
This usage is limited to mechanistically plausible cases. For example



is 13α-methyl-19-norpodocarpane rather than 19(4 → 13βH)abeopodocarpane. Further, it should not be used when "friedo" can be used equally well. Thus



is 9,5-friedo-10β- rather than 20(10 → 9R)abeo-5β-. However, "abeo" is preferred over "friedo" if its use results in fewer inverted centers requiring designation; for example

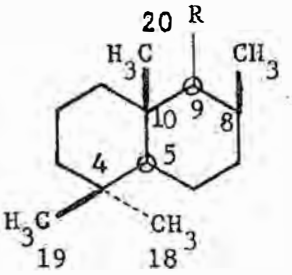


is 20(10 → 9R)abeoabietane, not 9,10-friedo-10β-abietane.

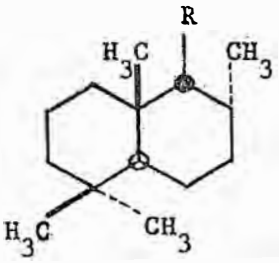
Friedo.--This designates one or more consecutive 1,2 migrations of alkyl groups and/or hydrogens around a ring system, but without affecting the ring system. This prefix is preceded by two locants. The first designates the carbon atom at which the rearrangement starts (presumably the position of the carbonium ion before rearrangement). The second designates the carbon atom at which the rearrangement stops (presumably by transoid addition of hydrogen to the carbonium ion after rearrangement). Migrating groups retain their original numbers, and the stereochemistry at the positions designated by the first and last locants and all intermediate positions is inverted in accord with biogenetic observations. Thus, the potential ROSANE skeleton becomes simply 8,5-friedopimarane.

The use of this modifier is the most radical of the suggestions in this nomenclature report. Most respondents were in favor of its use. It differs from abeo in two important respects. First, although like abeo it indicates a carbon bond migration, in most cases friedo will refer to a series of migrations. Second, unlike abeo, inversion of the stereochemistry at all affected centers is also involved. Friedo also only involves free alkyl groups and hydrogens and must not be used when one of the positions involved is a quarternary ring junction as C-8 in KAURANE, BEYERANE, and ATISANE. The alternative of an x-methyl-y-nor is far less satisfactory because of the difficulties introduced in defining stereochemistry.

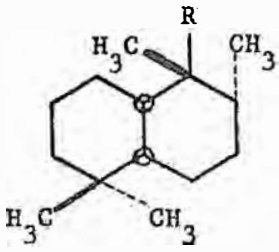
A number of examples of friedolabdanes is given below. It should be noted that since the migrations require inversion, only C-19 and not C-18 migrates. It also will be obvious that if a friedo operator can take two different paths, that path is preferred which involves the most highly substituted carbon atoms--usually ring junctions. As with abeo, friedo shall be limited to mechanistically plausible cases. Thus the first locant must designate a carbon substituted with a hydrogen before the friedo rearrangement, the second locant must designate a carbon substituted with a hydrogen after the friedo rearrangement. A friedo rearrangement which does not involve an alkyl group is named by designating the new stereochemistry alone.



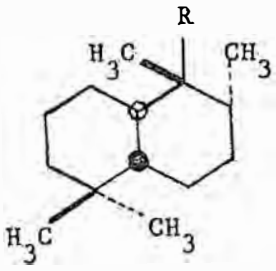
labdane



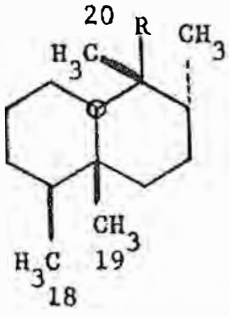
8α,9α-labdane
(not 8,9-friedolabdane)



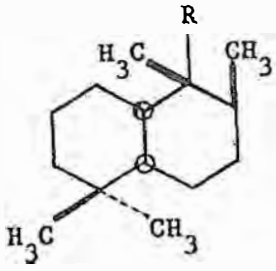
8,10-friedolabdane



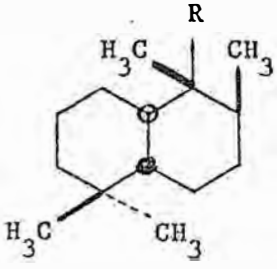
8,5-friedolabdane



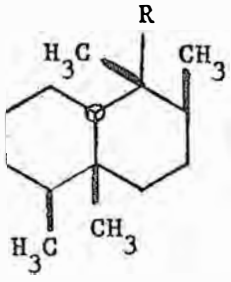
8α-clerodane
(not 8,4-friedolabdane)



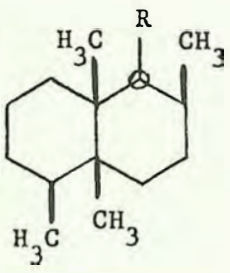
9,10-friedolabdane



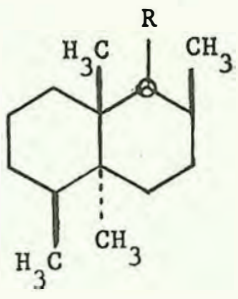
9,5-friedolabdane



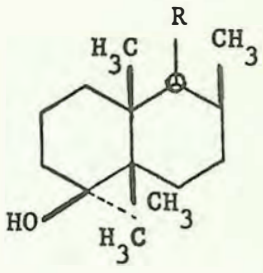
clerodane
(not 9,4-friedolabdane)



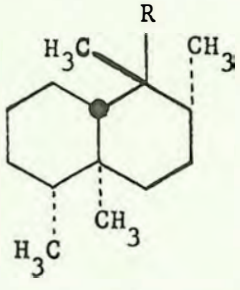
5,4-friedolabdane
(not 10,9-friedoclerodane)



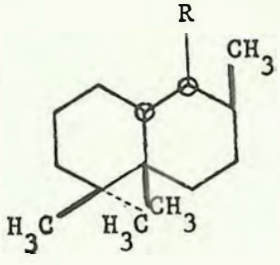
18(4 → 5)abeolabdane
(not 5,4-friedo-5α-labdane)



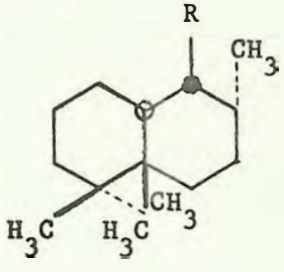
19(4 → 5)abeolabdan-4-ol
(not 5,4-friedolabdan-4β-ol)



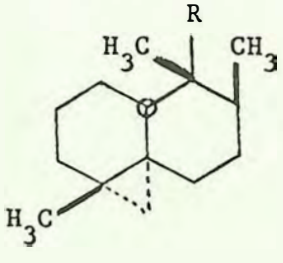
ent-9β-clerodane
(not ent-9,4-friedo-9β-labdane)



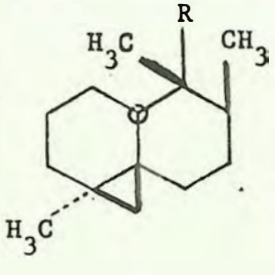
5,10-friedolabdane



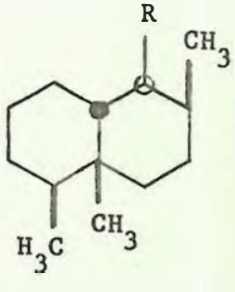
5,8-friedolabdane



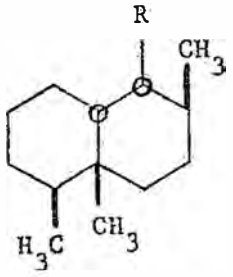
5,18-cyclo-9,10-friedolabdane



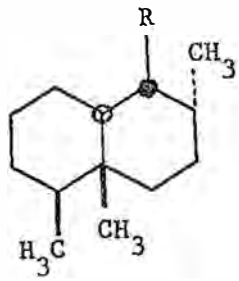
4β,19-cycloclerodane
(not 5,19-cyclo-9,5-friedolabdane)



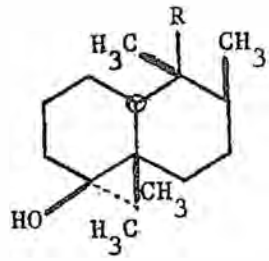
20-nor-9α,10β-clerodane
(not 20-nor-5,4-friedolabdane)



20-nor-9α-clerodane
(not 18-nor-5,10-friedolabdane)



20-nor-8α-clerodane
(not 18-nor-5,8-friedolabdane)



clerodan-4β-ol
(not 9,4-friedolabdan-4β-ol)

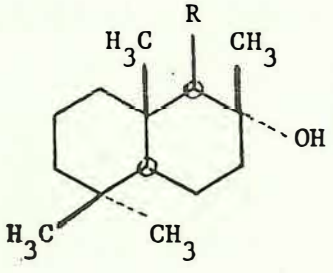
4. Designation of Stereochemistry of Parent Skeleton

The parent skeletons all possess the stereochemistry illustrated. The skeletons are numbered to correspond to accepted IUPAC practices, especially as related to the steroids, except that in certain cases this is slightly modified to maintain biogenetic interrelationships.

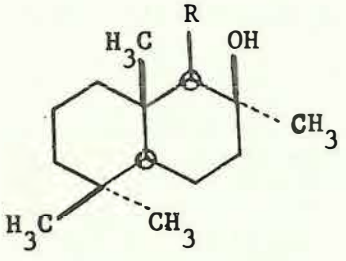
When a skeleton possesses inverted stereochemistry at one or more of the designated positions, the skeleton is first assigned to the normal or enantio series, and the inverted positions are then designated just before the skeletal name by the number and correct stereochemistry of the angular group, or the largest [according to the sequence rules (7)] of the secondary groups on a ring methylene. The side chain in LABDANE and CLERODANE is treated as part of the ring system. However, in the case of KAURANE, GIBBERELLANE, ATISANE, and BEYERANE, inversion of the stereochemistry at C-8 is not designated, this being implied in the stereochemistry of the other ring

junction at C-12 or C-13. Further, an 8α or 8β conveys no information in these skeletons since there are no angular groups there. In ACONANE, inversion of the C-17 bridge is indicated by specifying the inverted stereochemistry at C-7 only. Inversion of the C-15,16 bridge is indicated by specifying the inverted stereochemistry at both C-8 and C-13.

If an inversion can be adequately designated by specifying the stereochemistry of a substituent, this is preferable.



8-labdanol



8β-labdanol
(not 8α-labdan-8-ol)

It should be noted that in skeletons containing one or more secondary methyl groups, these methyl groups are usually oriented axially. This simplifies the nomenclature, since in the natural products there is usually either a double bond or a geminal equatorial hydroxyl at this position. It should be noted that hydrogenated natural products of this type will, therefore, often have the secondary methyl group in the epimeric equatorial position thus requiring designation of the inverted stereochemistry before the skeletal name.

These rules supersede our originally proposed use of "epi" to which a number of respondents objected. However, the use of "epi" in common names is still recommended.

As is the practice by Chemical Abstracts (which is also followed by IUPAC), if there is no locant specifying inverted stereochemistry just before the skeletal name and no nondetachable prefixes (which have accompanying locants), the first set of locants specifying unsaturation or if saturated the locants of the functional suffix group shall be placed just before the stem name.

5. Parent Hydrocarbons

The skeletons should always be drawn as shown so that α and β substituents on bridged rings will have stereochemical significance. In conformance with steroid rules, methyl groups, both angular and at the end of chains, shall be indicated by CH_3 (Me may be used in place of CH_3 if editorial conventions require it). In other words, bonds drawn with nothing indicated at the end are to be avoided. Hydrogen atoms at ring junctions are also to be shown. However, in this nomenclature we are also recommending adoption of the alternative and convenient system whereby the stereochemistry of hydrogen at ring junctions is indicated by an open (for αH) or closed (for βH) circle

as originally suggested by Linstead. As with the C-17 side chain in the steroids, the stereochemistry of a side chain of two or more carbon atoms is normally indicated solely by the assigned stereochemistry of the other group at this position.

Even though the resulting skeletons are not always the thermodynamically most stable form (as recommended by some respondents) or have all substituents β (as recommended by another), the skeletons now proposed are not only biogenetically consistent, but also turn out to be remarkably convenient to use, requiring fewer modifiers than would be the case otherwise.

The skeletons and their numbering are based on those given in McCrindle and Overton's review of diterpenes (9). [More recent reviews have been published by Fujita (61)]. Their system is logical and most closely approximates current usage. It is felt that new skeletons should be created only to satisfy future needs when two criteria have been met: (1) The presence of two or more modifiers of the parent skeleton or the use of one modifier two or more times (except nor), and (2) a substantial number of compounds with the same skeleton. New skeletons are also recommended when a substantial number of related compounds require abeo or friedo as a modifier.

PODOCARPANE.--An aromatic PODOCARPENE skeleton was originally suggested in response to criticism of naming dehydroabietic acid derivatives as

abietatrienes, and in a desire to emphasize the aromatic ring C found in a considerable number of related diterpenes. Many respondents commented on our choice of this skeleton; and although a few used such heartwarming adjectives as "brilliant" and "inspired," it is clear that a PODOCARPANE skeleton is definitely preferred by most respondents. The PODOCARPANE group will consist of only a few natural products, but will prove to be very useful in naming the numerous synthetic products being increasingly reported in the literature. Names based on PODOCARPANE should only be used when the resulting name is simpler than the corresponding name based on perhydrophenanthrene. In this skeleton, the numbering of the ring A angular methyl groups is 18, 19, and 20. Numbers 15, 16, and 17 are deleted so that correspondence with other diterpene skeletons is maintained.

We understand that there are moves afoot to distinguish steroids in which one or more rings are aromatic. If this is ever adopted in the steroids, it should also be extended to diterpenes such as those of the podocarpanes, totaranes, and abietanes which are aromatic. Hopefully, it will also be extendable to those labdanes with aromatic furan rings.

LABDANE.--The suggestion for a 13α-LABDANE and 13β-LABDANE met with only little approval and is therefore dropped in favor of a single LABDANE skeleton. Substituents at C-5, C-8, and C-13 are considered to be replacements of the hydrogen, and the stereochemistry of these substituents is not to be specified unless inverted.

According to the Fieser-Plattner method (6), the hydrogen at C-13 is α. Inversion at C-13 leading to the epimanool series of compounds will be indicated by a prefix just before the parent skeletal name of "13βH" unless there is a functional group at this position, in which case the inversion will be indicated as usual by specifying, for example, "13β-ol" rather than just "13-ol" as with the normal series. This method is preferred over the R and S system at this position because (1) the parent skeleton already includes the absolute stereochemistry at this position, and (2) the two groups of natural products related to the two stereochemistries at this position are not adequately differentiated by R and S.

The suggestion was made (59) that C-17 should be numbered 14 to correspond with the other skeletons, but this goes against IUPAC practice and leads to discontinuous numbering in the side chain. Carman has agreed. The lack of frequent interconversions between the labdane and other skeletons makes it far less desirable than, for example, in the group ATISANE-BEYERANE-KAURANE.

CLERODANE.--This new skeleton is 9,4-friedolabdane. It was chosen instead of COLUMBANE because of the latter's cis ring junction. Its use is limited to those compounds which would otherwise be named as 9,4-friedo- or 8,4-friedolabdanes, and the use of cycloclerodanes for naming corresponding

derivatives in the abietane or pimarane series is to be avoided. It is felt that although the "friedo" and "abeo" prefixes are valuable, they should be used to only a limited extent. This, together with the moderately large number of compounds of this group, led to the need for this skeleton.

PIMARANE and ISOPIMARANE.--The suggestion for a 13β-and 13α-PIMARANE skeleton met with little approval and is therefore dropped in favor of PIMARANE and ISOPIMARANE. It is, of course, impossible to decide whether a 17-methylpimarane is actually a 17-methylisopimarane. However, if such a case arises, the rule requiring the simpler nomenclature specifies the former name. As stated previously, the stereochemistry of side chains longer than methyl is not shown.

ABIETANE.--Fujita's suggestion (54) for this skeleton is adopted.

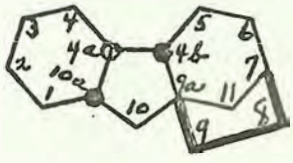
TOTARANE.--The suggestion of Cambie and Ito for a separate TOTARANE skeleton is adopted. There are many examples of this class, and it does represent a rather fundamental skeletal change. It is equivalent to 15(13 → 14βH)abeoabietane. The numbering stays the same as in ABIETANE.

TOTARANE also lends itself to the naming of a number of decanor triterpene bitter principles such as chaparrin, quassin, amarolide, and glaucarubin. However, the required diabeo prefix represents a mechanistically impossible rearrangement, and it is, therefore, not recommended that these compounds be named as totaranes.

CASSANE.--The stereochemistry at C-13 corresponds to ABIETANE. As before, the stereochemistry of the ethyl group is not indicated directly.

KAURANE.--C-13 and C-14 are shown to be above the plane of the rest of the molecules.

GIBBERELLANE.--Adoption of the suggestion (63) for the common nomenclature of the gibberellins is recommended. The need for a new parent skeleton for compounds of this type is apparent and has been recommended by many respondents. The current GIBBANE (80) skeleton is outside of the



systematic nomenclature so far proposed. Therefore, the suggested GIBBERELLANE [8(7 → 6βH)abeokaurane] is adopted on the advice of MacMillan, Takahashi, and others (27). This has the advantage of being systematic with the other skeletons and of including a complete stereochemical description. It will be noted that all examples given belong to the enantio series.

ATISANE.--Carbons 13 and 14 are placed to the right of 8 and 12 to clarify that substituents at 13 and 14 are oriented α and β in relation to the ring of carbons 8, 9, 11, 12, 13, and 14. Trachylobanes are considered to be cycloatisanes rather than cyclokauranes or cyclobeyeranes. Atisanes

are already a rather small group, and insufficient trachylobane derivatives are known to warrant a separate skeletal name at this time.

ACONANE.--This parent skeleton and its numbering were arrived at in joint discussions with Drs. O. E. Edwards, K. Wiesner, and S. W. Pelletier, and the proposal for this parent skeleton is adopted (62). It will be noted that all the diterpene alkaloids now can be included under this nomenclature system. The known diterpene alkaloids can be divided into three general groups: those based on KAURANE, those based on ATISANE, and those based on ACONANE. This skeleton is equal to 7β,20-cyclo-17-nor-9(8 → 15αH)abeo-8α-atisane. All diterpene alkaloids again appear to belong to the enantio series. However, the skeleton ACONANE is kept as shown to correspond to the other skeletons.

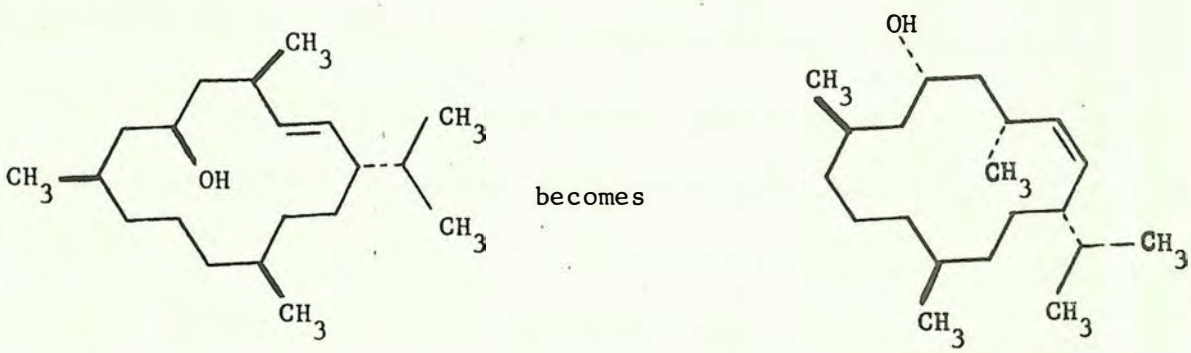
BEYERANE.--It should be noted that BEYERANE takes precedence over HIBANE (47). Therefore, it is also recommended that "beyerene" replace "hibaene," "stachene," and "cupressene."

TAXANE.--This skeleton is the one suggested (28).

A potential difficulty in the use of α,β-nomenclature in regard to taxane has been reported (10). It was pointed out that the Japanese use of the α,β-nomenclature is not fully consistent for the methyls we number 16 and 17. Thus it turns out that our C-16 is α to ring A and β to ring B, while C-17 is β to ring A and α to ring B. It was suggested that substituents at C-12, -13, and -14 be named as exo or endo while the C-15 methyls

are oriented α and β in relation to ring B. However, there is no need for confusion on this point. The way the TAXANE skeleton is drawn, carbons 1, 11, and 15 determine a plane with C-15 to the right. C-17 is clearly above this plane and therefore β, while C-16 is clearly below it and therefore α.

It should be noted that the previously postulated CEMBRANE skeleton is conformationally flexible and that introduction of a double bond can cause alterations in the way in which substituent groups are oriented. Thus, the Z isomer of E-2-cembren-6β-ol,



Therefore, the use of the α,β system of specifying stereochemistry is unsatisfactory and should be replaced by R,S. Further, the advantage of a skeleton with proscribed stereochemistry of the alkyl substituents is diminished; also the rule prohibiting drawing parent skeletons in other ways is impractical here. Therefore, it is recommended that cembrane derivatives be named as 3,7,11,15-tetramethyl-1,14-cyclohexadecanes

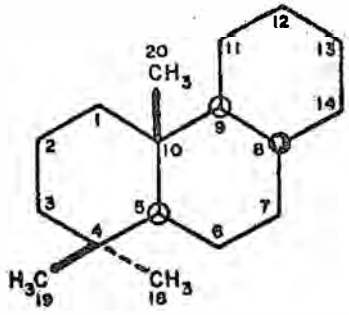
according to standard IUPAC nomenclature rules with the stereochemistry of all substituents specified by R, S, or ξ. The alternative 2,6,10,14-tetramethyl-3,16-cyclohexadecane name should not be used even if it results in a lower number for the functional groups so that all cembrane derivatives will be indexed together. Disecotaxane names are also to be avoided. Thunbergene is historically correct and therefore preferable to cembrene which was later shown to be the same compound (23). Therefore, common names based on "thunbergane" are preferable to ones based on "cembrane" or "duvane."

6. Double Bonds

Unsaturation is indicated in the usual way. The use of "Δ" before the name is not recommended except, perhaps, in common names. The stereoisomerism of the double bond must be specified if there are alternative possibilities. Double bonds within cyclohexane rings will, of course, never have alternative possibilities. This stereoisomerism should be designated according to the new system of Chemical Abstracts (68) in which substituents on the double bond are classified by the Cahn, Ingold, Prelog rules. If the higher priority groups on each of the double-bonded carbon atoms are on the same side, the stereochemical descriptor "Z-" (from the German zusammen) is used. If they are on opposite sides, the stereochemical descriptor "E-"(from the German entgegen) is placed just

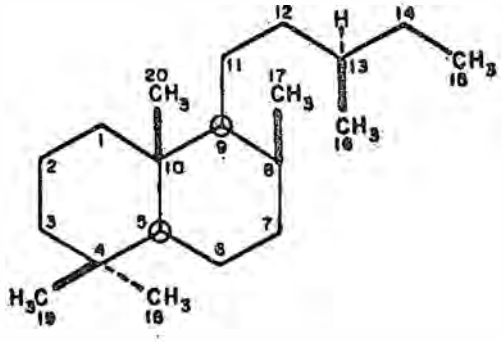
before the locant. (See cis- and trans-communic acids.) A mixture of double bond stereoisomers can be named by using "EZ-". This parallels our use of "αβ" to indicate a mixture of stereoisomers at one position (see manool trihydrochloride).

Alternatively when there can be no misunderstanding, "cis-" or "trans-" can be placed just before the appropriate locant. When more than one such is present, this may be shortened to "c-" or "t-." Although "cis" and "trans" are normally preferred by IUPAC over "E" and "Z," the common occurrence of trisubstituted double bonds in the diterpenes favors use of the latter system. Unknown stereoisomerism is indicated by "ξ-" before the locant.



PODOCARPANE

12-hydroxy-8,11,13-podocarpatrien-16-oic acid	podocarpic acid
12-hydroxy-13-methyl-8,11,13-podocarpatrien-7-one	nimbiol



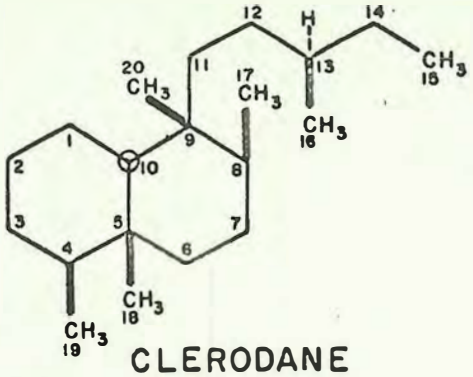
LABDANE

8(17),Z-12,14-labdatriene	cis-biformene (12)
8(17),13(16),14-labdatriene	sclarene
8β,13αβ,15-trichlorolabdane	manool trihydrochloride (32)
8(17),14-labdadien-13-ol	manool
ent-8(17),14-labdadien-13β-ol	ent-13-epimanool (13) ((—)-epimanool)
Z-12,14-labdadien-8-ol	abienol (14)

13(16),14-labdadien-8-ol	isoabienol (31)
14-labdene-8,13-diol	sclareol
8(17),14-labdadiene-6α,13β-diol	larixol
ent-6β-acetoxy-8(17),Z-12,14-labdatrien-18-oic acid	6β-acetoxyozic acid (zanzibaric acid)
ent-8(17),Z-12,14-labdatrien-18-oic acid	ozic acid (66)
8(17),E-12,14-labdatrien-19-oic acid	trans-communic acid (elliotinoic acid)
8(17),Z-12,14-labdatrien-19-ol	cis-communol
methyl 15,16-dihydroxy-8(17),E-13-labdadien-19-oate	methyl sciadopate
8(17),14-labdadiene-13,19-diol	torulosol
8(17),14-labdadiene-13β,19-diol	13-epitorulosol (72)
13-hydroxy-8(17),14-labdadien-19-oic acid	torulosic acid (15) (cupressic acid)
8(17),E-13-labdadiene-15,19-diol	agathadiol
15-hydroxy-8(17),E-13-labdadien-19-al	isoagatholal (16) (contortolal)
19-hydroxy-8(17),E-13-labdadien-15-oic acid	agatholic acid
8(17),E-13-labdadiene-15,19-dioic acid	agathic acid
ent-13βH-labd-8(17)-ene-15,19-dioic acid	oliveric acid
8(17)-labdene-15,18-dioic acid	pinifolic acid
7-labden-15-oic acid	cativic acid
8-hydroxy-15-labdanoic acid	labdanolic acid
8(17),E-13-labdadien-15-oic acid	anti-copalic acid (epicopalic acid)

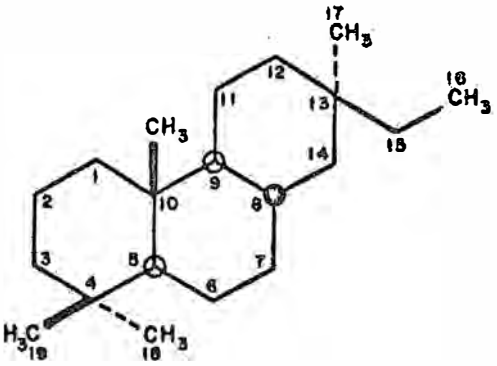
14,15,16-trinorlabdan-13,8-olide	ambreinolide
ent-13βH-labd-8(17)-en-15-oic acid	eperuic acid
ent-3β-14ξ,19-trihydroxy-8(17),12-labdadien-16,15-olide	andrographolide (36)
ent-8,13β-epoxy-14-labdene	ent-13-epimanoyl oxide (olearyl oxide)[2]
8,13-epoxy-3-norlabd-14-en-2-one	colensenone
9ξ,13β-epoxy-7-labden-15-oic acid	grindelic acid
8,12S-epoxy-13-labden-15,12-olide	α-levantenolide
15,16-epoxy-8̊(17),13(16),14-labdatrien-19-oic acid	anti-daniellic acid (lambertianic acid)
ent-15,16-epoxy-8(17),13(16),14-labdatrien-18-oic acid	polyalthic acid
dimethyl 15,16-epoxy-12-oxo-8(17),13(16),14-labdatriene-19,20-dioate	dimethyl sciadinonate
12S,20:15,16-diepoxy-8(17),13(16),14-labdatrien-19,20-olide	sciadin
8(17)-labdene-15,19-diol	imbricatadiol (73)
8,12R,15-nitrilo-5,4-friedolabda-3,13-dien-19-ol	thelepogine
ent-3β-bromo-E-13-labdene-8β,15-diol	aplysin-20 (44)
15,16-epoxy-9-hydroxy-7,13(16),14-labdatrien-6-one	solidagenone (27)
ent-15,16-epoxy-8(17),13(16),14-labdatriene-6α,19-diol	psiadiol (41)
15,16-epoxy-9-hydroxy-8α-labda-13(16),14-dien-19,6β-olide	marrubiin (53)

[2]Although this name actually has historical precedence, the more systematic common name has been preferred by most chemists.

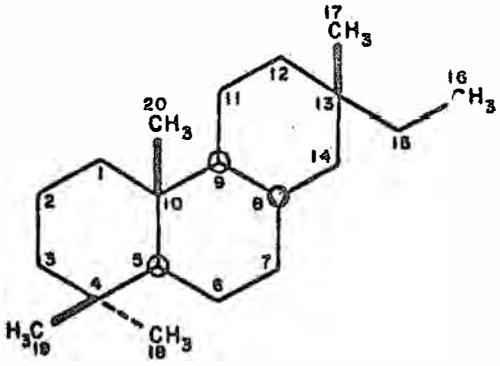


CLERODANE

ent-3,13-clerodadien-15-ol	kolavenol (76)
12ξ-hydroxy-3,13-clerodadiene-18,19:15,16-diolide (?)	olearin (67)
ent-7β-acetoxy-15,16-epoxy-3β,4,12S-trihydroxy-13(16),14-clerodadien-20-al	cascarillin A (11)
4β,18:11R,16R:15,16-triepoxy-13βH-clerod-14-en-6β,19-diol diacetate	clerodin
15,16-epoxy-4-hydroxy-5α,8α-cleroda-2,13(16),14-triene-17,12S:18,1β-diolide	columbin (tinosporin)
ent-3-oxo-18-norcleroda-13(16),14-dien-20,12S-olide (assuming stereochemistry is related to cascarillin A)	crotonin (35)
ent-2α,3α:15,16-diepoxy-4-hydroxy-5α-cleroda-7,13(16),14-triene-17,12R:18,1β-diolide	fibraurin (43)
ent-15,16-epoxy-19-hydroxy-3,13(16),14-clerodatrien-18-oic acid	hautriwaic acid (57)
15,16-epoxy-3,13(16),14-clerodatrien-18-oic acid (?)	hardwickiic acid
ent-8,12R:15,16-diepoxy-20-nor-5α,10β-cleroda-13(16),14-diene-17,6β:18,2β-diolide	diosbulbin B (78)



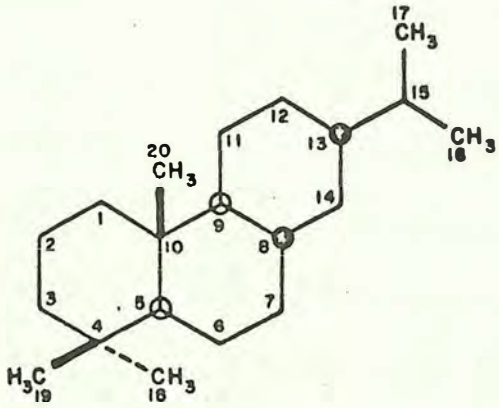
PIMARANE



ISOPIMARANE

8(14),15-pimaradien-18-oic acid	pimaric acid (dextropimaric acid)
8(14),15-pimaradien-18-ol	pimarol (pimarinol)
8(14),15-pimaradien-18-al	pimaral (pimarinal, cryptopinone)
8(14),15-isopimaradien-18-oic acid	sandaracopimaric acid
7,15-isopimaradien-18-oic acid	isopimaric acid (isodextropimaric acid)
7,15-isopimaradien-18-ol	isopimarol (isopimarinol)
3β,16-dihydroxy-7-isopimarene-2,15-dione	araucarolone
ent-8(14)-pimarene-3β,15ξ,16-triol	darutigenol
8,4-friedoisopimara-4(18),15-diene	dolabradiene
ent-8,4-friedopimar-4(18)-ene-15ξ,16-diol	erythroxydiol Y
ent-5,19-cyclo-8,5-friedopimara-11β,15S,16-triol	erythroxytriol Q (33)
ent-5,19-cyclo-8,5-friedopimar-15-ene	devadarene
7-oxo-8,10-friedopimar-15-en-19,10β-olide	rosenonolactone
8,5-friedoisopimara-5,15-diene	rimuene

2α-hydroxy-8,5-friedopimara-5(10),15-dien-19-oic acid	isorosenolic acid
ent-8(14),15-pimaradiene-3β,19-diol	oblongifoliol (79)

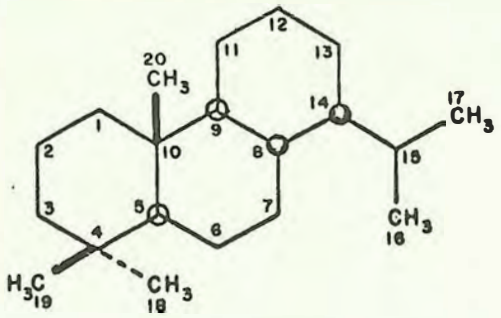


ABIETANE

7,13-abietadien-18-oic acid	abietic acid
7,13-abietadien-18-ol	abietol (abietinol)
8,13-abietadien-18-oic acid	palustric acid
8,13-abietadien-18-ol	palustrol[3]
8(14),13(15)-abietadien-18-oic acid	neoabietic acid
8(14),12-abietadien-18-oic acid	levopimaric acid (sapietic acid)
18-norabietane	fichtelite
8,11,13-abietatrien-19-oic acid	4-epidehydroabietic acid (callitrisic acid (58))

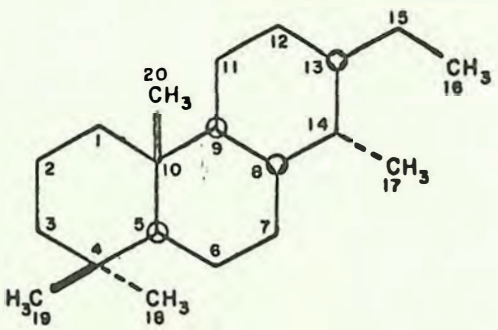
[3] Drs. Herout and Sorm have kindly agreed to change the name of their sesquiterpene, palustrol, (1) to sesquipalustrol.

8,11,13-abietatrien-18-oic acid	dehydroabietic acid
8,11,13-abietatrien-18-ol	dehydroabietol (dehydroabietinol)
11-hydroxy-7,9(11),13-abietatriene-6,12-dione	taxodione (24)
8,11,13-abietatrien-12-ol	ferruginol
8,11,13-abietatriene-3,12-diol	hinokiol
12-hydroxy-6,8,12-abietatriene-11,14-dione	dehydroroyleanone
12-hydroxy-8,11,13-abietatrien-7-one	sugiol
11,12-dihydroxy-8,11,13-abietatrien-20-oic acid	carnosic acid (salvin)
11,12-dihydroxy-8,11,13-abietatrien-20,7-olide	carnosol (picrosalvin)
15(13 → 12)abeoabieta-8,11,13-trien-13-ol	semperviro1 (16)
12-hydroxy-5β-abieta-8,11,13-triene-6,7-dione	xanthoperol
11,15-dihydroxy-5,7,9(11),13-abietatetraen-12-one	fuerstione (39)
12ξ,13ξ-epoxy-15-hydroxy-8-abietene-7,11-dione	callicarpone (37)
13ξ,13ξ'-dihydroxy-[8ξ,11ξ':14ξ,14ξ'-biabieta]-8',9(11)-diene-12,12'-dione	maytenone (60)
3,9-dimethylphenanthro[1,2-b]furano-4,5-quinone (NOT 14,16-epoxy-19,20-dinorabieta-1,3,5,7,9,13,15-heptaene-11,12-dione)	tanshinone I (38)
14,16-epoxy-20-nor-13ξ-abieta-5,7,9,13-tetraene-11,12-dione (NOT 2,3,4,7,8,9-hexahydro-3ξ,9,9-trimethylphenanthro[1,2-b]furano-4,5-quinone or 4,4,17ξ-trimethyl-15-oxagona-5,7,9,13-tetraene-11,12-dione)	cryptoshinone (38)



TOTARANE

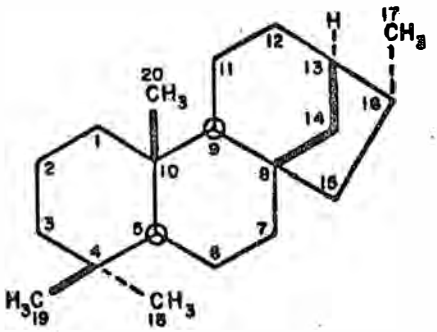
8,11,13-totaratrien-13-ol	totarol
12,12'-bi-8,11,13-totaratrien-13-ol	bitotarol (podototarin)
12,12'-bi-13-hydroxy-8,11,13-totaratrien-19-oic acid	macrophyllic acid (17)
1α,2α:7α,8α-diepoxy-3β,15S-dihydroxy-13,17-dinortotar-9(11)-ene-12,14R:19,6β-diolide	inumakilactone A (74)



CASSANE

3β-hydroxy-7-oxo-E-13(15)-cassen-16-oic acid	cassaic acid
19-O-methyl hydrogen 7-oxo-E-13(15)-cassene-16,19-dioate	cassamic acid

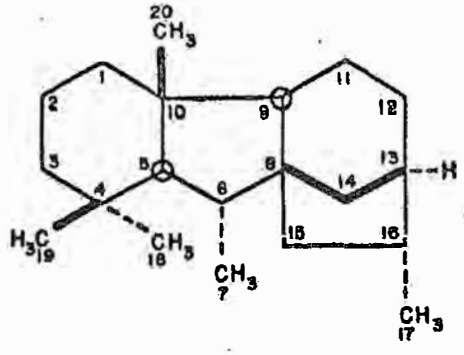
β-N,N-dimethylaminoethyl 3β,7β-dihydroxy-E-13(15)-cassen-16-oate	cassaidine
12,16-epoxy-12,15-cassadien-18-oic acid	vinhaticoic acid
12,16-epoxy-12,15-cassadien-19-oic acid	vouacapenic acid
16-O-β-N,N-dimethylaminoethyl 19-O-methyl 6α-hydroxy-7-oxo-E-13(15)-cassene-16,19-dioate	erythrophleguine
1α,2α-diacetoxy-12,16-epoxy-12,15-cassadiene-5,14-diol	ε-caesalpin (56)



KAURANE

16-kaurene	kaurene ((+)-kaurene, mirene)
ent-16-kaurene	ent-kaurene ((—)-kaurene)
13β-kaur-16-ene	phyllocladene
ent-6α,16,17-kauranetriol	corymbol
ent-13-hydroxy-16-kauren-19-oic acid	steviol
ent-3,19-epoxy-18,4-friedokaura-3,18-diene-16,17-diol	cafestol
ent-3,19-epoxy-18,4-friedokaura-1,3,18-triene-16,17-diol	kahweol

ent-6β,20-epoxy-3α,6α-dihydroxy-15-oxo-6,7-secokaur-16-en-7,1β-olide	enmein (18) (isodonin)
ent-6α,15α-diacetoxy-7β,20-epoxy-16-kaurene-1α,7α-diol	trichokaurin (19)
ent-6,7-secokaur-16-ene-6,7,19-trioic acid 6,19-anhydride	fujenoic acid
ent-5(10 → 1β)abeokaur-10(20)-ene-3β,5,6α,14α,16-pentaol	grayanotoxin II (42)
ent-7β,20-epoxy-1β,6α,7α,14α-tetrahydroxy-16-kauren-15-one	oridonin (20)
ent-2α,15β-dihydroxy-18-norkaur-16-en-19-oic acid	atractyligenin (21)
ent-16,17-dihydroxy-3-kauranone	abbeokutone (52)
ent-19-O,19-N,20-N-β-oxyethylimino-16-kauren-15β-ol	garryine
ent-19-N,20-N,20-O-β-oxyethylimino-16-kauren-15β-ol	veatchine
ent-15α-acetoxy-16-kauren-19-oic acid	xylopic acid (71)
ent-6,20-epoxy-6S,11-dihydroxy-15-keto-6,7-secokaur-16-en-7:1β-olide	nodosin (77)
ent-5,16-kauradien-19-oic acid	grandiflorenic acid (25)
ent-16-kauren-19-al	espelal (25)
ent-15β,16-epoxy-7α,18-kaurandiol	sideroxol (25)



GIBBERELLANE

ent-3α,10,13-trihydroxy-20-norgibberella-1,16-diene-7,19-dioic acid 19,10-lactone

ent-3α,13-dihydroxy-16-gibberellene-7,19-dioic acid

ent-10,13-dihydroxy-20-norgibberell-16-ene-7,19-dioic acid 19,10-lactone

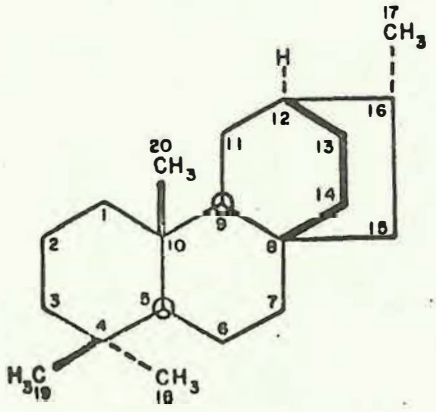
ent-3α,13-dihydroxy-20-oxo-16-gibberellene-7,19-dioic acid

gibberellin A_3
(gibberellic acid)

gibberellin A_{18}
(Lupinus gibberellin I)

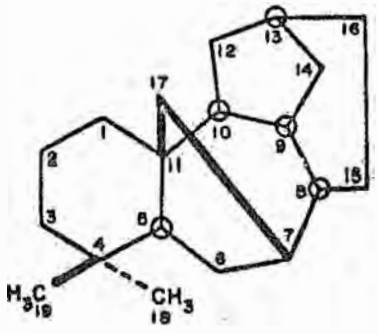
gibberellin A_{20}
(Pharbitis gibberellin)

gibberellin A_{23}
(Lupinus gibberellin II)



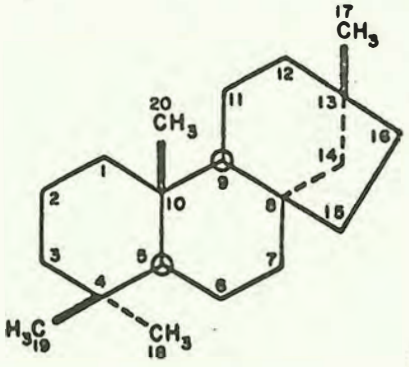
ATISANE

ent-16-atisene	atisirene
ent-13α,16-cycloatisane	trachylobane
ent-13α,16-cycloatisan-18-oic acid	trachylobanic acid
7β,20-epoxy-19,20-β-hydroxyethylimino-16-atisen-15α-ol	ajaconine
ent-6,19,20-nitrilo-14,20-cycloatis-16-ene-2β,11β,13β-triol	hetisine (48) (delatine)
ent-19-N,20-N,20-O-β-oxyethylimino-16-atisen-15α-ol	atisine
ent-6α-hydroxy-6,19,20-nitrilo-14,20-cycloatis-16-en-11-one	spiradine A (70)



ACONANE

ent-14β-acetoxy-17,19-ethylimino-16α,18-dimethoxy-1β,8-aconanediol	condelphine (50)
ent-8-acetoxy-14β-benzoyloxy-17,19-ethylimino-1α,6β,16α,18-tetramethoxy-3β,13,15β-aconanetriol	aconitine (49)
ent-17,19-ethylimino-1α,6α,14β,16α-tetramethoxy-7,8,18-aconanetriol	lycoctonine (51)



BEYERANE

ent-15-beyerene

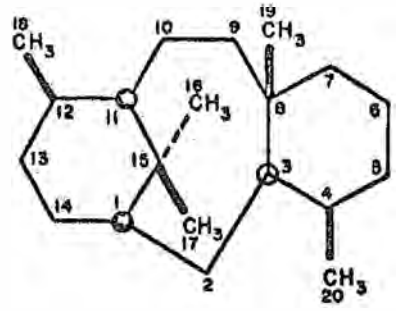
beyerene
[(+)-hibaene (22), stachene, (+)-cupressene]

ent-15-beyeren-19-ol

monogynol

ent-15-beyerene-3β,17,19-triol

beyerol



TAXANE

1,2α,5α,9α,10β-pentahydroxy-4(20),11-taxadien-13-one	taxicin I (30)
2α,9α,10β-triacetoxy-13-oxo-4(20),11-taxadien-5α-yl R-β-dimethylamino-β-phenylpropionate	taxine II (30)
3,8-secotaxa-E-3,E-7-dien-12-ol (?)	verticillol (29)
2α,5α,9α,10β-tetraacetoxy-3,11α-cyclotax-4(20)-en-13-one	taxinine-L (55)

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APPENDIX

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THE COMMON AND SYSTEMATIC NOMENCLATURE OF CYCLIC DITERPENES

Prepared by

JOHN W. ROWE

Cosponsored by:

J. ApSimon, M. Fëtizon, E. Fujita, L. Gough, W. Herz, P. R. Jefferies, D. Mangoni, T. Norin, K. Overton, S. W. Pelletier, and E. Wenkert

Addenda and Corrigenda to
Third Revision

February 1969

FOR REVIEW ONLY

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P. 7, l. 10: Correct the spelling of "Steroid."

P. 7, l. 18: The sentence "The skeleton ... in this report." should be a footnote of "phorbol (34)" on l. 13.

P. 8, l. 15 and 16: The sentence should be changed to read: "Therefore, ATISANE is arbitrarily chosen and trachylobanes should be named with this skeleton as has been done."

P. 11, item 2: The part of item 2 on this page should be replaced with:

"Standard IUPAC rules are followed. Fused ring systems unless otherwise designated are considered to be in the plane of the paper. Bonds projecting above this plane in the normal series are indicated by a heavy line and designated "β." Bonds projecting below this plane are indicated by a dotted line and designated "α." In the enantiomeric series, these will, of course, be reversed (i.e., ent-α = β). To avoid confusion as to the stereochemistry of substituents on rings which must be shown as being above or below the plane of the paper, these substituents shall be designated by the R and S convention (7). Positions so affected are C-14 in KAURANE, BEYERANE, and GIBBERELLANE, C-13 and -14 in ATISANE, and C-17 in ACONANE.

"Because of the occurrence of cyclized derivatives, the R and S convention is preferable for designating the stereochemistry at positions in side chains to the α,β convention of the Fieser-Plattner method (6). However, the R and S designation at C-13 in LABDANE and CLERODANE is undesirable since there are two distinct series, and modifications of C-14 and C-16 can change the R and S assignments even within one series. Furthermore, the LABDANE and CLERODANE skeletons carry the absolute stereochemistry at C-13 with them. An example of the difficulties inherent in using R and S at C-13 in LABDANE can be illustrated by labdanolic and eperuic acids. In both compounds C-13 is actually S (ent-13R in eperuic acid). However, the parent hydrocarbon of both is R. It should be noted that R and S refer to the absolute stereochemistry in the normal series. In the enantiomeric series, the absolute configuration is the opposite of that assigned (i.e., ent-R = S)." Continue on page 12 without change.

P. 15, l. 7 and 9: Change "is" to "was."

P. 16: The first sentence after "Friedo.--" should read: "This designates one or more consecutive 1,2 migrations of axial alkyl groups and hydrogens around a ring system, ..."

P. 20, l. 7 of item 4: After "When a skeleton possesses inverted stereochemistry" insert "not already specified by the locants of modifiers ...."

P. 20, l. 11 of item 4: This line should be changed to read: "group, or the preferred (largest) [according to the sequence rules (7)] of the ...."

P. 22, l. 12: After the first sentence of item 5 insert "Compounds in the enantiomeric series should also be drawn as shown, but with the stereochemistry at all positions reversed. α,β,R, and S will then have opposite meaning from their use in the normal series (see page 11)." "In conformance ...." should then be the beginning of a new paragraph.

P. 22, l. 2 from bottom: At the end of the line insert "and only hydrogen."

P. 23, l. 4: At the end of the paragraph, add "This eliminates confusion in the representation of the stereochemistry of the first side chain carbon, i.e., C-11 in LABDANE and CLERODANE, and C-15 in PIMARANE, ISOPIMARANE, ABIETANE, TOTARANE, and CASSANE. The point of attachment of such side chains is, therefore, treated like a ring junction."

P. 23, l. 15: The "only" should be placed after "future needs."

P. 29, l. 3 under formulas: "Proscribed" should be changed to "prescribed."

P. 29, last line: Change "3,7,11,15-tetramethyl-1,14-cyclohexadecanes" to "1-isopropyl-4,8,12-trimethylcyclotetradecanes."

P. 32: Podocarpic acid should be "... 19-oic acid."

P. 33, l. 4: The preferred common name is "zanibaric acid (85)" which has an ent-6α-acetoxy group.

P. 34: Grindelic acid (83) should be "9,13β-epoxy ..."

P. 34: Thelepogine (84) should be "8,12S,15-nitrilo ..."

P. 35: The numbers "18" and "19" on the CLERODANE skeleton should be reversed.

P. 35: Olearin should be "rel-12ξ-hydroxy-3,13-clerodadiene-15,16:18,19-diolide." The question mark after the name can be removed.

P. 35: The third compound is "cascarillin," not "cascarillin A."

P. 35: Crotonin should be "ent-15,16-epoxy-3-oxo ..." Its stereochemistry is assumed to be related to cascarillin.

P. 35: Fibraurin should be "2β,3β:15,16-diepoxy ... diolide," a member of the normal series.

P. 35: Hardwickiic acid (76) should have its systematic name prefaced by "ent-." The question mark after the name can be removed.

P. 36: The number "20" was omitted from the formula of PIMARANE.

P. 37: Reference "58" should be placed after "4-epidehydroabietic acid" rather than after "callitrisic acid."

P. 38: Hinokiol should be "... -3β,12-diol."

P. 38: The last compound is "cryptotanshinone" and is a 20-nor-15ξ-abietane derivative. The first incorrect name for this compound should be "2,3,6,7,8,9-hexahydro ... quinone."

P. 39: Inumakilactone A was incorrectly named. It should be "1α,2α:7α,8α-diepoxy-3β,13S-dihydroxy-13-methyl-12,13-secopodocarp-9(11)-ene-12,14R:19,6β-diolide."

P. 40: Cafestol and kahweol should both be 19(4 → 18)abeokauranes rather than 18,4-friedokauranes since the rearrangement involves a position (C-18) not part of the ring system.

P. 41: Enmein should be "ent-6S,20-epoxy-3α,6-dihydroxy ..."

P. 41: Grayanotoxin II should be "ent-5(10 → 1αH)abeokaur-10(20)ene-3α,5,6α,14S,16-pentaol."

P. 41: Oridonin should be "14S" rather than "14α."

P. 41: Garryine (62) should be "ent-19S-O,19-N, ..."

P. 41: Veatchine (62) should be "ent-19-N,20R-N,20-O-β- ..."

P. 41: "Xylopic acid" should be placed in parentheses since the original discoverer (82) gave only a systematic name as recommended.

P. 41: Nodosin should be "ent-6S,20-epoxy-6,11β-dihydroxy-15-oxo-6,7-secokaur-16-en-7,1β-olide."

P. 43: Trachylobane and trachylobanic acid should both be "13R" instead of "13α."

P. 43: Ajaconine (62) should be "ent-7β,20S-epoxy ... 15α-ol."

P. 43: Hetisine should be "ent-6β,19,20S-nitrilo-14S,20- ... triol."

P. 43: Atisine (62) should be "ent-19-N,20S-N, ... 15α-ol."

P. 43: Spiradine A should be "ent-6α-hydroxy-6β,19,20S-nitrilo-14S,20-cycloatis-16-en-11-one."

P. 44: An αH should be shown on the drawing at C-7.

P. 44: Condelphine and aconitine have an "ent-17S,19-ethylimino" group.

P. 44: Lycoctonine has an "ent-17R,19-ethylimino" group.

P. 45: Add "15-beyerene" "hibaene (46) [(—)-hibaene]."

P. 45: Ent-15-beyerene should have the preferred common name of "ent-hibaene (22)."

P. 45: The common name "erythroxylol A (81)" is preferred over "monogynol."

Literature Cited

Ref. 9: The first author's name is spelled "Raphael." The page numbers are "47-113."

Ref. 10: The journal should be "J. Chem. Soc. (C)."

Ref. 18: The third author's name is "K. Fuji."

Ref. 19: The correct page numbers are "148, 466."

Ref. 22: Rutledge's initials are "P. S." Add "R. D. H. Murray and R. McCrindle, Chem. and Ind. 1964, 500."

Ref. 23: Thiessen's initials are "W. E."

Ref. 30: The journal is "J. Chem. Soc. (C)."

Ref. 34: The last reference should be expanded to read: "R. C. Petersen, G. Ferguson, L. Crombie, M. L. Games, and D. J. Pointer, Chem. Commun., 1967, 716."

Ref. 38: The second author is "Thompson." The journal is "J. Chem. Soc. (C)."

Ref. 41: The last author's initial is "C."

Ref. 42: The second author is "T. Kozima."

Ref. 46: Replace reference with "Y. Kitahara and A. Yoshikoshi, Abstracts of the 6th Natural Products Symposium of the Japanese Chemical Society, Sapporo, Japan, July 6-7, 1962, pp. 113-119; Tetrahedron Letters, 1964, 1771."

Ref. 54: The correct page number is "968."

Ref. 56: The second author is "K. Bjåmer."

Ref. 58: Add "R. M. Carman and H. C. Deeth, Aust. J. Chem. 20, 2789 (1967)."

Ref. 62: The second author's initials are "L. H." The book is now in press.

Add "81. R. McCrindle, A. Martin, and R. D. H. Murray, J. Chem. Soc. (C), 1968, 2349."

Add "82. J. R. Cannon, P. N. Chow, P. R. Jefferies, and G. V. Meehan, Aust. J. Chem. 19, 861 (1966)."

Add "83. L. Mangoni and M. Belardini, Gazz. Chim. It. 93, 455 (1963); L. Mangoni and M. Adinolfi, ibid. 97, 66 (1967)."

Add "84. J. Fridrichsons and A. McL. Mathieson, Acta Cryst. 16, 206 (1963)."

Add "85. G. Hugel and G. Ourisson, Bull. Soc. Chim. France 1965, 2903."

P. 55: Professor Mangoni's initial is "L," not "D."

P. 57: Add the following names and addresses:

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